

# (12) UK Patent Application (19) GB (11) 2 306 344 (13) A

(43) Date of A Publication 07.05.1997

(21) Application No 9521840.0

(22) Date of Filing 25.10.1995

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(51) INT CL<sup>6</sup>  
C07C 29/16 , B01J 31/30

(52) UK CL (Edition O )  
B1E E1142 E1180 E1252 E1260 E1302 E1311 E1322  
E1412 E1431 E1451 E1454 E1473 E1601  
U1S S1515

(56) Documents Cited  
WO 95/05354 A1 US 5144068 A

(58) Field of Search  
UK CL (Edition O ) B1E  
INT CL<sup>6</sup> B01J 27/128 27/13 31/28 , C07C 29/16 45/50  
51/14  
Online databases: WPI and CLAIMS

(54) Catalysed hydroformylation

(57) Ethylenically unsaturated compounds are reacted with carbon monoxide and hydrogen in the presence of a catalyst.

The catalyst components are:-

- a) a source of Group VIII metal cations - preferably a palladium salt,
- b) a source of anions, other than halide ions; the preferred source being trifluoromethane sulphonic acid,
- c) a source of bidentate ligands of formula:



wherein:- M<sup>1</sup> and M<sup>2</sup> are, independently, PAs and Sb,

R is a 1-4 atom bridge,

R<sup>1</sup> and R<sup>2</sup> together represent a bivalent cyclic group, as may

R<sup>3</sup> and R<sup>4</sup>, which may also be independent hydrocarbyl groups, and

d) is a iodide of an alkali or alkaline-earth metal.

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Fig. 1

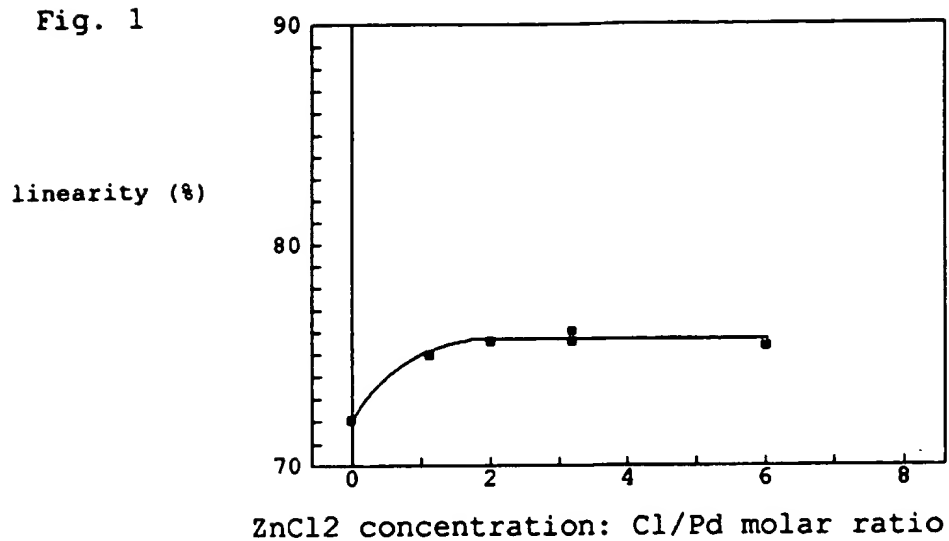


Fig. 2

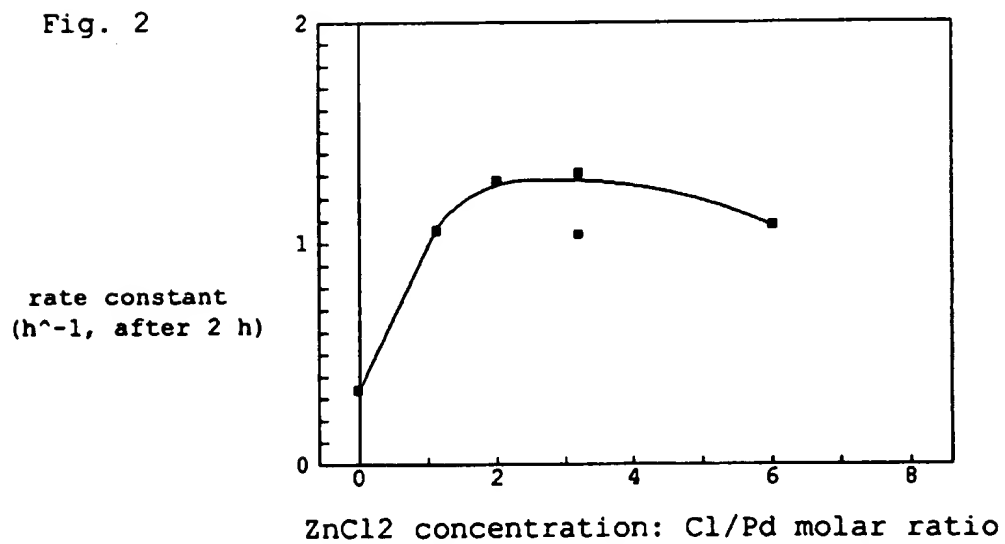


Fig. 3

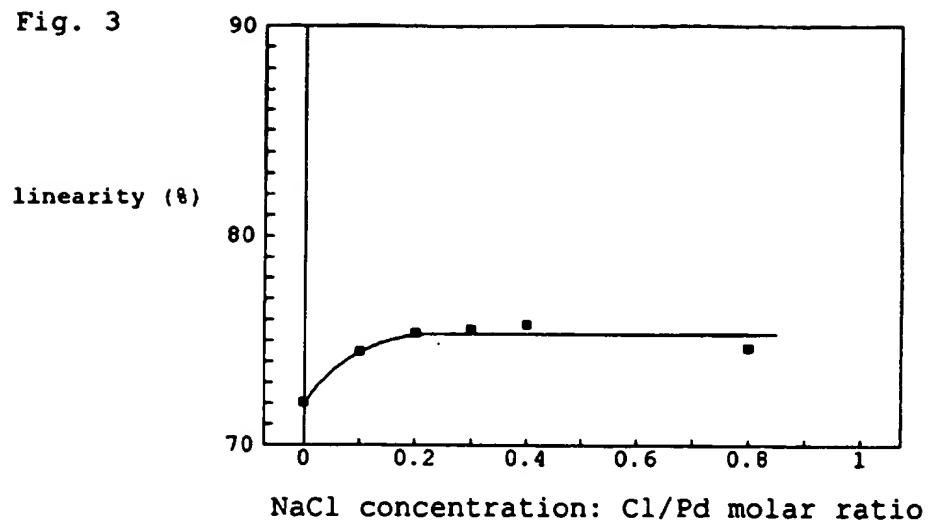


Fig. 4

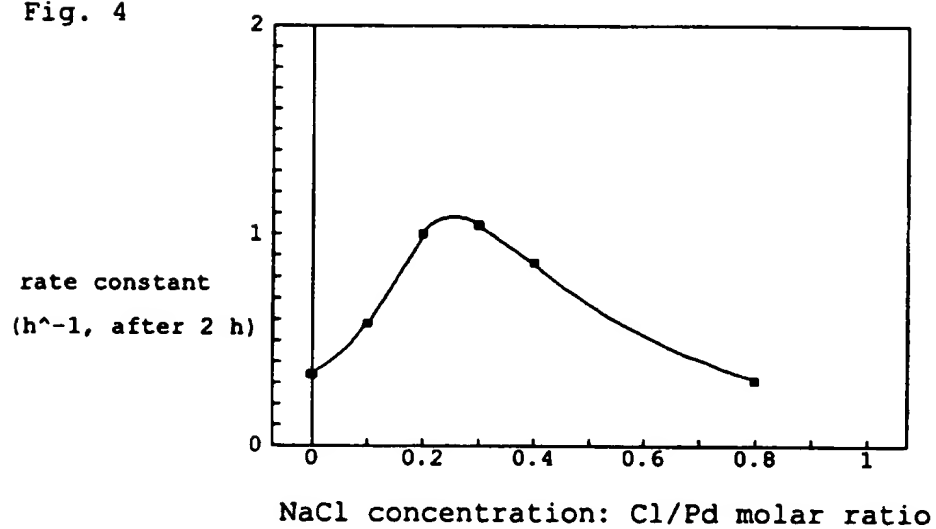


Fig. 5

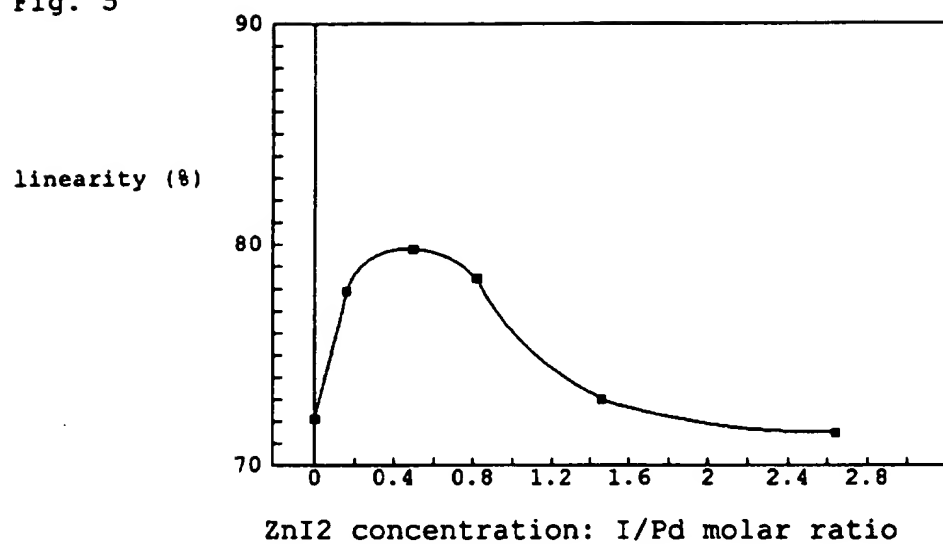


Fig. 6

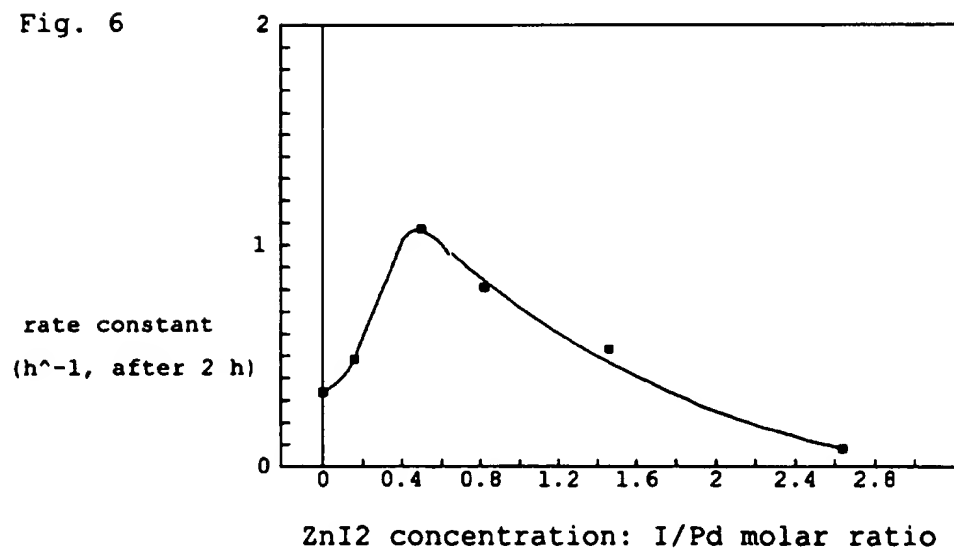


Fig. 7

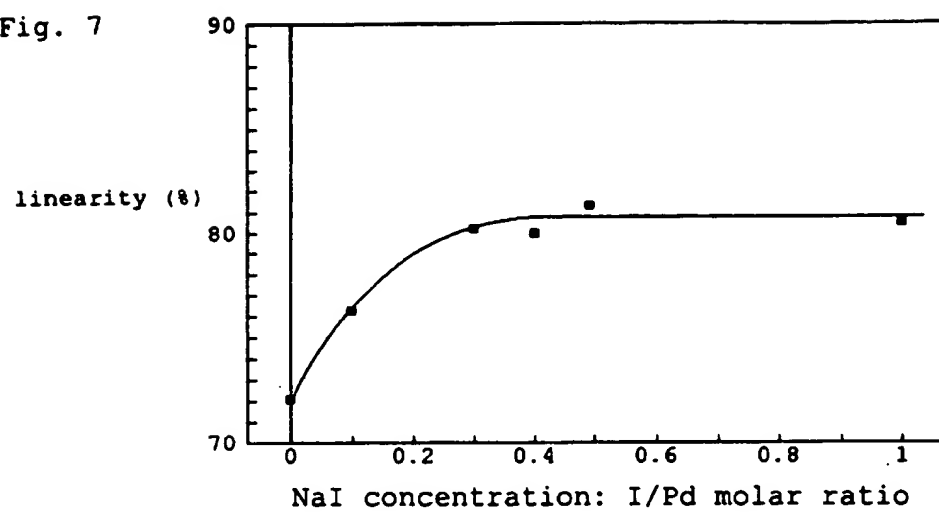
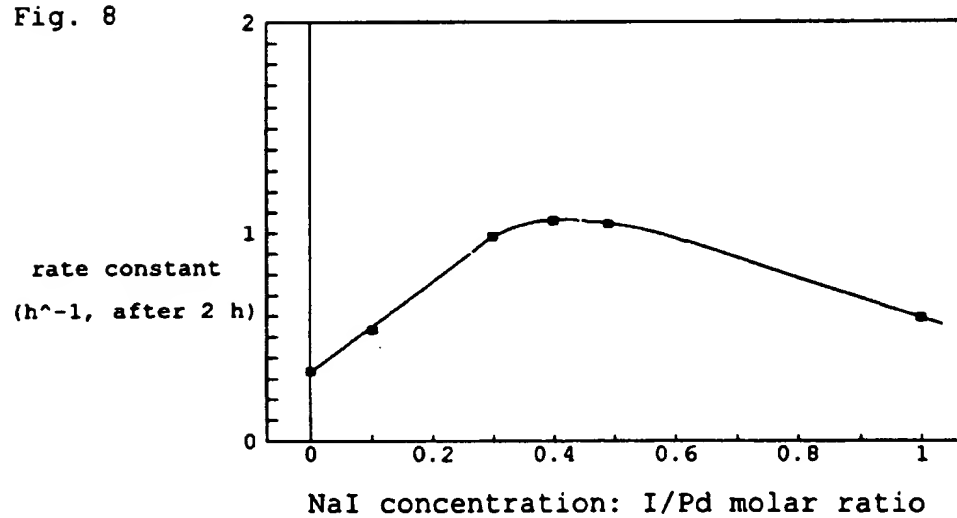


Fig. 8



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# HYDROFORMYLATION PROCESS

The invention relates to a process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst.

5       The hydroformylation of ethylenically unsaturated compounds, to form oxo-aldehydes and/or oxo-alcohols, hereinafter referred to as oxo-products, is of considerable industrial importance. The process has been in commercial operation for decades and over the years  
10       much development work has been done to optimise the reaction conditions, the catalyst system and the equipment. Although significant progress regarding higher yield and selectivity to the desired reaction products has been made, it is felt that in some aspects further  
15       improvement of the process is still needed.

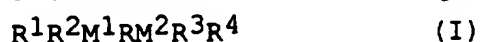
      In International application WO 95/05354 a process is disclosed wherein excellent yields and selectivity's towards hydroformylation products are achieved. In particular the use of a source of halide anions, more in  
20       particular chloride anions, as catalyst promoter besides the catalyst system was found very advantageous. However, the linearity of the hydroformylation products so produced, especially when the Group VIII metal component is a palladium cation leaves, reaches only about 70% (cf.  
25       Table III of WO 95/05354) for C<sub>15</sub> oxo-products. On the other hand, commercial oxo-alcohols tend to have a linearity in the order of 80%. It hence is desirable to further improve the process of WO 95/05354 in this regard.

30       Surprisingly, it has now been found that the process

of WO 95/05354 may be improved as regards the linearity by selection of a specific iodide source as catalyst promoter.

Accordingly, the present invention provides a process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

- a) a source of Group VIII metal cations;
- b) a source of anions, other than halide anions;
- c) a source of bidentate ligands of the formula



wherein  $M^1$  and  $M^2$  independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1 to 4 atoms in the bridge,  $R^1$  and  $R^2$  together represent a bivalent substituted or non-substituted cyclic group whereby the two free valences are linked to  $M^1$  and  $R^3$  and  $R^4$  independently represent a substituted or non-substituted hydrocarbyl group, or together represent a bivalent substituted or non-substituted cyclic group whereby the two free valences are linked to  $M^2$ ; and

- d) a source of halide anions as catalyst promoter in a molar ratio between halide anion and Group VIII metal cation of at most 5:1, characterised in that the source of halide anions is an alkali metal iodide or earth-alkaline metal iodide, preferably sodium and/or potassium iodide.

In WO 95/05354 both hydrogen halides, e.g., HCl, HBr and HI, and metal halides, e.g., NaCl, MgBr<sub>2</sub>, ZnCl<sub>2</sub>, ZnI<sub>2</sub>, KBr, RbCl, CsCl, CsI, MgI<sub>2</sub> and CuCl have been mentioned. Indeed, in Table III and VI examples are given of hydroformylations in the presence of several hydrogen halides and some of the aforementioned metal halides. These examples support the preference for hydrogen chloride and metal chlorides over the corresponding

iodides in view of the better rate of reaction. That equal rate and better linearity could be obtained with alkali metal iodides, in particular sodium iodide, could not be learned from this International application.

5       The ethylenically unsaturated compound, used as starting material, is preferably an olefin having from 2 to 30 carbon atoms per molecule, or a mixture thereof. It may comprise one or more double bonds per molecule. Preferred are internal olefins having from 4 to 24 carbon  
10       atoms, or mixtures thereof. Such olefin mixtures are commercially readily available as products of a process for the oligomerization of ethylene, followed by a double bond isomerization and disproportionation reaction. Typical examples are mixtures of linear internal C<sub>6</sub> to  
15       C<sub>8</sub> olefins, of linear internal C<sub>11</sub> to C<sub>12</sub> olefins and of linear internal C<sub>13</sub> to C<sub>14</sub> olefins.

Carbon monoxide and hydrogen may be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 5:1 to 1:5, typically 3:1 to 1:3. Preferably  
20       they are supplied in a ratio within the range of 2:1 to 1:2.

In the present specification the metals of Group VIII are identified by their symbol as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt. Preferred are the metals of the platinum  
25       group, i.e., Ni, Pd and Pt. Of these, palladium is most preferred. Examples of suitable metal sources are compounds such as salts of the metal and nitric acid, sulphuric acid, sulphonic acids, or carboxylic acids with up to 12 carbon atoms; metal complexes, e.g. with carbon  
30       monoxide or acetylacetonate; or the metal combined with a solid material such as an ion exchanger or carbon. Palladium(II) acetate and platinum(II) acetylacetonate are examples of preferred metal sources.

As component (b), any compound generating these non-  
35       halide anions may be used. Such compounds may comprise



acids or salts thereof. For example, any of the acids mentioned above, which may also participate in the salts of the Group VIII metals, may be used. The anions are preferably derived from strong acids, i.e., acids having a pKa value of less than 3, preferably less than 2 as measured in aqueous solution at 18 °C. The anions derived from these acids are non-coordinating or weakly coordinating with the Group VIII metals.

Typical examples of suitable anions are anions of phosphoric acid, sulphuric acid, sulphonic acids and halogenated carboxylic acids such as trifluoroacetic acid. Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such as  $\text{BF}_3$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$ ,  $\text{AlCl}_3$ ,  $\text{SnF}_2$ ,  $\text{Sn}(\text{CF}_3\text{SO}_3)_2$ ,  $\text{SnCl}_2$  or  $\text{GeCl}_2$ , with a protic acid, such as a sulphonic acid, e.g.  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{CH}_3\text{SO}_3\text{H}$  or a hydrohalogenic acid such as  $\text{HF}$  or  $\text{HCl}$ , or a combination of a Lewis acid with an alcohol. Examples of such complex anions are  $\text{BF}_4^-$ ,  $\text{SnCl}_3^-$ ,  $[\text{SnCl}_2.\text{CF}_3\text{SO}_3]^-$  and  $\text{PF}_6^-$ . The preferred anion source for a Pd-based catalyst is trifluoromethanesulphonic acid.

The bidentate ligands of formula (I), i.e., component c) of the catalyst system, is preferably selected from 1,2-bis(1,4-cyclooctylenephosphino)ethane, 1,2-bis(1,5-cyclooctylenephosphino)ethane and mixtures thereof; in which case  $\text{M}^1$  and  $\text{M}^2$  are both phosphorus atoms, R is composed of two carbon atoms and both  $\text{R}^1$  together with  $\text{R}^2$  and  $\text{R}^3$  together with  $\text{R}^4$ , represent a 1,4- or 1,5-cyclooctylene group. Alternative bidentate ligands have been described in the International application mentioned above, subject-matter of which is incorporated by reference. For the preparation of the bidentate ligands, reference is made to known techniques, for example the method disclosed in GB-A-1,127,965.

The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually

amounts in the range of  $10^{-8}$  to  $10^{-1}$ , preferably in the range of  $10^{-7}$  to  $10^{-2}$  mole atom of Group VIII metal per mole of ethylenically unsaturated compound are used. The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of Group VIII metal from 0.5 to 6, preferably from 1 to 2 moles of bidentate ligand are used, and from 0.5 to 15, preferably from 1 to 8 moles of anion source or a complex anion source (i.e., component b) are used.

Preferably, the molar ratio between dissociated iodide anions and Group VIII metal cations is at most 3:1, since a too high concentration of iodide may lead to catalyst poisoning. More preferably, the molar ratio is less than 1:1, for instance from 0.02:1 to 1:1. Very good results have been achieved at a molar ratio ranging from 0.25:1 to 0.6:1.

The hydroformylation can be suitably carried out at moderate reaction conditions. Hence temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction pressures in the range of 1 to 300 bar abs are suitable, but in the range of 5 to 100 bar abs are preferred. Lower or higher pressures may be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

In the process of the invention, the ethylenically unsaturated starting material and the formed hydroformylation product may act as reaction diluent. Conveniently, however, the hydroformylation reaction may be carried out in the additional presence of a solvent such as sulfolane.

The process of the invention is eminently suitable to be used for the preparation of alcohols from internal olefins at high rate, in particular by using a catalyst

system as defined above, based on palladium as Group VII metal.

The invention will be illustrated by the non-limiting examples, as described hereinafter.

5     Comparative Examples A - C, Example 1

Four sets of experiments were carried out using  $\text{ZnCl}_2$  (Comp. A),  $\text{NaCl}$  (Comp. B),  $\text{ZnI}_2$  (Comp. C), that are known from WO 95/05354, and  $\text{NaI}$  as catalyst promoter. The experiments were conducted in a 300 ml magnetically stirred autoclave ("Hastelloy", a trademark) at 105 °C and 50 bar abs (hydrogen gas/carbon monoxide ratio of 2:1 v/v). The autoclave was charged with 62 ml of an internal  $\text{C}_{11}$ - $\text{C}_{12}$  olefin (40%  $\text{C}_{11}$ , 60%  $\text{C}_{12}$ , ex. SHELL), 50 ml of 2-ethylhexanol, 0.6 ml water and 13 ml sulfolane (including 0.39 mmol of palladium(II) acetate, 0.55 mmol of diphosphine (90% isomeric pure 1,2-bis(1,5-cyclo-octylenephosphino)ethane) 0.91 mmol of trifluoromethanesulphonic acid and varying amounts of halide-containing catalyst promoter. As a consequence, the Pd concentration in the reactor was 3.1 mmol/l, and the molar ratio of palladium(II) acetate, diphosphine and trifluoromethanesulphonic acid was 1:1.4:2.3.

The reaction was followed by means of GC. Typically, at virtual complete conversion (better than 99%) an overall alcohol yield of around 98% was observed. By-products are paraffin and, at incomplete conversion, aldehydes and heavy ends of the acetal type. Linearity (ratio n over n and branched in percent) was also determined by GC. Kinetic analysis provided pseudo first-order rate constants.

Further details and analytical results are compiled in the following sets of figures. Of these, Figures 1, 3, 5 and 7 illustrate the linearity of the alcohol at varying amounts of the catalyst promoter, expressed as molar ratio of halide over metal. Figures 2, 4, 6 and 8

display the rate constant as a function of the relative amount of catalyst promoter.

As can be seen from Figs. 2 and 4,  $\text{Cl}^-$ -based catalyst promoters provide a good activity (highest first-order rate constant of more than  $1 \text{ hr}^{-1}$ ), although  $\text{ZnCl}_2$  at a wider operating window. However, as shown in Figs. 1 and 3, linearity remains around 75% for all amounts of promoter tested. Paraffin make was slightly lower for  $\text{ZnCl}_2$ .

Ignoring the difference in price and the amount needed to promote the reaction,  $\text{ZnCl}_2$ , rather than  $\text{NaCl}$  is the preferred  $\text{Cl}^-$ -based catalyst promoter.

Turning now to Fig. 6, an activity is found for  $\text{ZnI}_2$  that is comparable to that of  $\text{NaCl}$ . A linearity of about 80% is achievable, however, only at a I/Pd molar ratio of 0.5. Using an I/Pd molar ratio of 0.3 or 0.8, linearity was down to 78%. Paraffin make for  $\text{ZnI}_2$  is excellent (only traces of paraffins found), albeit that the concentration of heavy ends and aldehydes is substantially higher than in the previous experiments.

Figs. 7 and 8 illustrate the performance of a catalyst promoter according to the present invention. A linearity of 80% is reached at a relatively low I/Pd molar ratio of 0.3, and is maintained for higher ratios. The activity peaks at a slightly higher concentration than in Fig. 3, but the decline in activity at either side of the maximum is substantially less. The behaviour regarding byproducts is similar to that of  $\text{ZnI}_2$  in respect of the paraffin make and similar to that of  $\text{NaCl}$  in respect of the occurrence of aldehydes and heavy ends.

Experiments with  $\text{F}^-$ -based catalyst promoters showed no promoting effect, whereas  $\text{Br}^-$ -based catalyst promoters showed behaviour as regards linearity and other properties similar to  $\text{Cl}^-$ -based catalyst promoters.

These experiments demonstrate that alkali or earth-

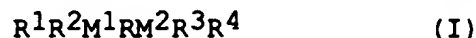
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alkaline metal iodides are the preferred catalyst promoters to obtain linearities of around 80% from the range of catalyst promoters mentioned in WO 95/05354.

C L A I M S

1. A process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

- 5 a) a source of Group VIII metal cations;  
b) a source of anions, other than halide anions;  
c) a source of bidentate ligands of the formula



wherein  $M^1$  and  $M^2$  independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent  
10 bridging group containing from 1 to 4 atoms in the bridge,  $R^1$  and  $R^2$  together represent a bivalent substituted or non-substituted cyclic group whereby the two free valences are linked to  $M^1$  and  $R^3$  and  $R^4$   
15 independently represent a substituted or non-substituted hydrocarbyl group, or together represent a bivalent substituted or non-substituted cyclic group whereby the two free valences are linked to  $M^2$ ; and  
d) a source of halide anions as catalyst promoter in a  
20 molar ratio between halide anion and Group VIII metal cation of at most 5:1, characterised in that the source of halide anions is an alkali and/or earth-alkaline metal iodide.

2. A process as claimed in claim 1, wherein the  
25 ethylenically unsaturated compound is a linear internal olefin having from 4 to 24 carbon atoms.

3. A process as claimed in claim 1 or 2, wherein carbon monoxide and hydrogen are supplied in a ratio within the range of 5:1 to 1:5.

30 4. A process as claimed in any one of claims 1 to 3, wherein component a) of the catalyst system is a

palladium salt.

5. A process as claimed in any one of claims 1 to 4, wherein component b) of the catalyst system is a trifluoromethanesulphonic acid.

5 6. A process as claimed in any one of claims 1 to 5, wherein component c) of the catalyst system is selected from 1,2-bis(1,4-cyclooctylenephosphino)ethane, 1,2-bis(1,5-cyclooctylenephosphino)ethane and mixtures thereof.

10 7. A process as claimed in any one of claims 1 to 6, wherein the source of halide anions consists of sodium and/or potassium iodide.

8. A process as claimed in claim 7, wherein the molar ratio between halide and Group VIII metal cations is in  
15 the range from 0.02:1 to 1:1.

9. A process as claimed in claim 7, wherein the molar ratio between halide and Group VIII metal cations is in the range from 0.25:1 to 0.6:1.



Application No: GB 9521840.0  
Claims searched: 1-9

Examiner: John Warren  
Date of search: 13 December 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): B1E

Int CI (Ed.6): C07C 29/16, 45/50, 51/14; B01J 27/128, 27/13, 31/28

Other: Online databases: WPI and CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	WO 95/05354 A1 SHELL - see Claims 1 and 6	
A	US 5,144,068 HOECHST - see Column 4 lines 22-38	

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
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A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.